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GRAVITATIONAL EFFECTS ON COMBUSTION SYNTHESIS OF ADVANCED POROUS MATERIALS

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Abstract

Combustion Synthesis (self-Propagating high-temperature synthesis-SHS) of porous Ti-TiB_x composite materials has been studied with respect to the sensitivity to the SHS reaction parameters of stoichiometry, green density, gasifying agents, ambient pressure, diluents and gravity. The main objective of this reseach program is to engineer the required porosity and mechanical properties into the composite materials to meet the requirements of a consumer, such as for the application of bone replacement materials. Gravity serves to restrict the gas expansion and the liquid movement during SHS reaction. As a result, gravitational forces affect the microstructure and properties of the SHS products. Reacting these SHS systems in low gravity in the KC-135 aircraft has extended the ability to form porous products. This paper will emphasize the effects of gravity (low g, 1g and 2g) on the SHS reaction process, and the microstructure and properties of the porous composite. Some of biomedical results are also discussed.

Keywords: composite, porous material, combustion synthesis, microgavity, bone replacement.

Introduction

Production of highly porous composites by traditional materials processing is limited by difficult and often time consuming processing techniques. However, combustion synthesis or self-propagating high temperature synthesis (SHS) allows many ceramics, intermetallic and metallic systems to be rapidly formed with relative ease. The primary advantage of SHS is based on rapid kinetics and favorable energetics, simple reagents, and therefore low material cost [1]. The SHS reaction processing conditions are associated extremely fast heating rates and cooling rates (up to 10^5-10^6K/s), high temperatures (2500-3500K) and short reaction times (on the order of a few seconds). These conditions have the attractive potential to yield advanced materials with novel structures and properties. The porosity of product results largely from the initial porosity in the compressed, unreacted "green" pellet and the volume change that takes place between the product and reactant species during the combustion synthesis reaction. If the combustion temperature exceeds the melting point of the product, product densification can take place due to solidification. Such a process can be used to produce ceramic and cermet materials with the total porosity of 30-50% [2]. The structure and properties of materials produced by SHS are strongly dependent upon the reaction parameters of the combustion reaction [3]. The main reaction parameters that control combustion synthesis reactions are reaction stoichiometry, reactant particle size, green density, the presence and use of diluents or inert reactants, and pre-heating of the reactants. These parameters will affect the exothermicity of the reaction, the control of the ignition and combustion temperatures, thereby affecting the microstructure and properties of the synthesized materials. A number of conditions must be satisfied in order to obtain high porosity materials: an optimal amount of liquid and solid phases must be present in the combustion front; a gas must be evolved simultaneously (but not interfere) with the liquid phase formation; and the combustion reaction must propagate at a high velocity [4]. If the gas is generated at the combustion front and is coincident with the generation of low viscosity (high plasticity) liquid, the gas may pass through the liquid and produce open pores. However, if the liquid generated at the combustion front has a high viscosity, an increasing amount of closed pores may result. There needs to be a maximum amount of open pores at the surface of a bone replacement material in order to facilitate rapid bone growth [5,6]. Therefore, a balance of gas generation while maximizing liquid generation of sufficiently high plasticity at the combustion front must be created by the SHS reaction to successfully engineer a bone replacement material system. Conducting combustion systhesis reaction in low gravity has extended the ability to form porous products [7,8]. The convective heat transfer mechanisms which operate in normal gravity, 1g, constrain the combustion synthesis reactions. Gravity also acts to limit the porosity that may be formed as the force of gravity serves to restrict the gas expansion and the liquid movement during the reaction. The overall understanding and control of these parameters in combustion synthesis can be used to synthesize engineered porous materials to meet the property requirements of bone replacement materials. Advanced porous materials implants offer the possibility for bone ingrowth as well as a permanent structural framework for the long-term replacement of bone defects.

Results and Discussion

The recent research conducted at the Colorado School of Mines (CSM) the SHS of porous metal-matrix composites has been concerned with reactions based on the Ti-TiB_x system:

$$(y+z)\ \mathrm{Ti} + xz\ \mathrm{B} = y\ \mathrm{Ti} + z\ \mathrm{TiB_x} \quad .$$

Porous titanium alloys have been identified as a surgical implant material for a quarter of a century like Ti6-Al4-V, Ti13Nb13Zr [9]. The selection of these Ti alloy systems is based on the observation that the factors of product pore size and microstructure, production scale-up cost, profit potential, and environmental and health issue are all positive. Previous results conducted on the combustion synthesis of porous Ti-TiB_x composites at CSM have shown the pore size can range from 100 m to 1000 m, while the product porosity can range from 30% to 70%. Reacting this reaction system under low gravity showed that the ceramic particle size may be controlled using gravity conditions.

Effect of Gravity

The porous SHS product is also sensitive to the external forces present during the reaction. One of the external forces is gravity. Gravity retards the expansion of the porous SHS product. Brief exposure (20 sec) to variable gravity as provided by parabolic flights in the NASA KC-135 aircraft allows examination of gravitational forces. Conducting these SHS reactions under low gravity conditions (~0.2g) tends to lead to higher combustion temperatures, larger pore size, more even pores, different microstructures and pore size distributions. Increasing the gravity vector increases the force acting against the expanding gases generated near the reaction front resulting in decreased expansion or "foaming" of the reaction system. As shown in Figure 1, this effect may lead to an increased combustion temperature, T_c, on the increase of the gravitational force since heat loss to the pores decreases [10].

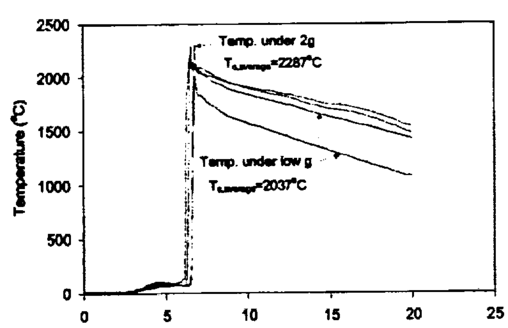

Figure 1: Effect of Gravity on Combustion Temperature.

Also, as shown in Figure 2 and Figure 3, decreasing the gravity force yields a more even pore size and distribution of the large pores.

(a) Under high g

(b) Under low g

Figure 2. Photomacrographs of the reacted samples of the same green pellet conducted under (a) low gravity and (b) 2g. The reactant composition is 44.93% atomic percent boron.

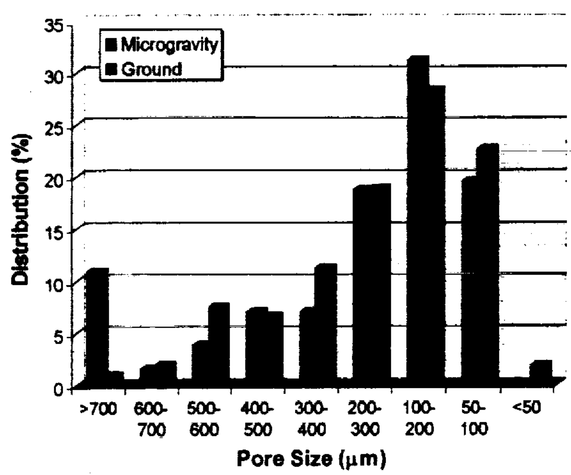

Figure 3. Pore size distributions under microgravity and ground condition.

Since the gas could be released from the combustion front freely without gravitational force, the effect of gas to form pore at the combustion front would increase. This effect may cause the porosity of product increase under low gravity condition. As shown in Figure 4, the porosity of low gravity condition is always higher than that of under high gravity condition.

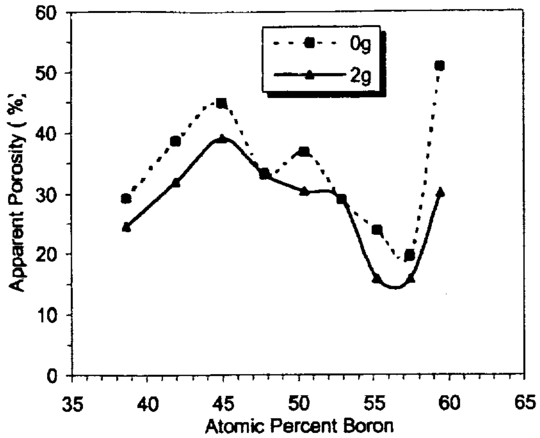

Figure 4. Gravity effect on porosity of $Ti-TiB_x$ SHS products.

Biomedical Test Results

Figure 5 indicates that the elastic modulus of the $Ti-TiB_x$ system studied in this report (44.9% boron or $8\%Ti-92\%TiB_x$) is 5.8Gpa. It is proposed that the $Ti-TiB_x$ system produced via the combustion synthesis route can be engineered to be more compatible with natural bone, having an elastic modulus of 12-20 GPa. The possible engineering approaches are control of the reaction composition, structure, and infiltration of the porous $Ti-TiB_x$ composite with a biocompatible polymer. Additionally, this system possesses the advantage of near net shaping and machinability as illustrated in Figure 6. This will benefit further machining to final shape for bone implant applications.

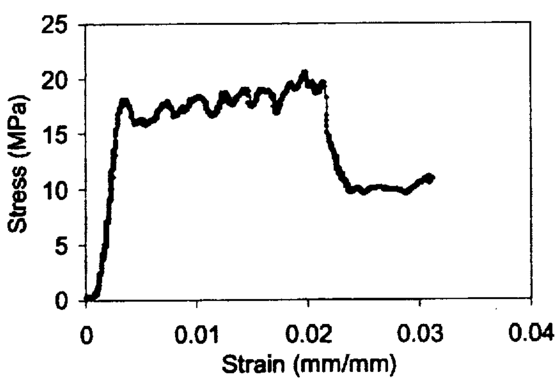

Figure 5. Stress-strain curve of a product with 92% TiB and 8% Ti.

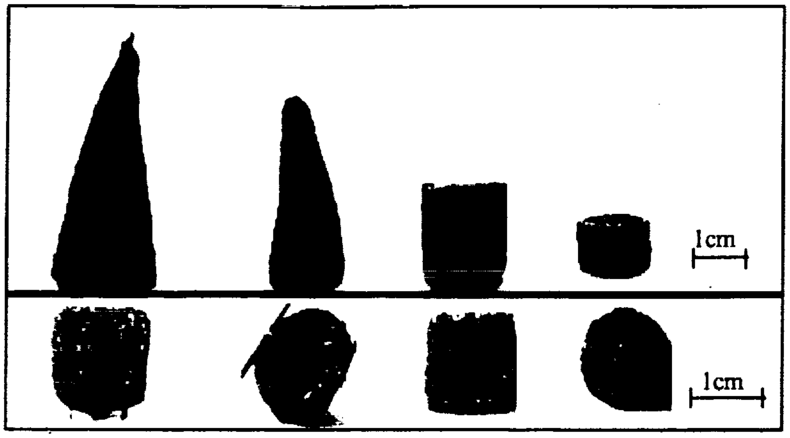

Figure 6. Near net shaping of $Ti\text{-}TiB_x$ products (as reacted).

Three groups of $Ti\text{-}TiB_x$ samples were studied using skull onlay implant tests into rat skulls. The primary goal of rat skull onlay tests is to identify a synthetic composition to improve and better control the osteoinductive response of permanent Ti-TiB implants for skeletal regeneration. This study will specifically determine whether the porous Ti-TiB metal matrix composite materials are biocompatible, and positive bioactive. The osteogenic activity of the implants will be evaluated using accepted protocols for X-ray mineral density, fluorescent labeling and histology (3 weeks). The results will be used to determine the material combinations required for optimal osteogenic performance and to assess their clinical potential.

Table 1 presents the weight change results of the rats during the 4 weeks of implant surgery. One of these porous samples fused to the skull of the rat, which is an extremely positive result. Some of the samples were also with a bone protein addition made to the porous $Ti\text{-}TiB_x$ materials in an effort to improve the regeneration process. The samples with the BP (Bone Protein) addition also fused to the skull of the rats. Both of these sets of data indicate strongly that there is some considerable natural bone ingrowth with no apparent immune response.

Conclusions

The results presented in this paper demonstrate that gravity is an important parameter for controlling the combustion temperature, porosity, pore size and microstructure in the $Ti\text{-}TiB_x$ SHS system. Decreasing the gravity decreases combustion temperature; increases pore size and porosity; and changes the pore size distribution and microstructure. Controlling the SHS reaction parameters, porous bodies of a variety of matrix combinations can be formed with a reproducible amount of porosity and microstructural features. In addition, the preliminary biomedical test results show that the porous Ti-TiB composite material is a potential bone replacement material that could be used as a permanent structural framework applications.

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Table 1. The change of rat weight 4 weeks after the implant surgery

Type of Sample	Sample I.D.	Weight @ implant (g)	Weight @ explant (g)
Pure porous Ti-TiB samples	1-1	144	203
	1-2	163	242
	1-3	144	200
	1-4	151	205
	1-5	147	196
Samples with 7mg collagen	2-1	142	202
	2-2	139	195
	2-3	149	196
	2-4	152	208
	2-5	145	191
Samples with 7mg collagen & 35□g BP-99067	3-1	157	211
	3-2	151	206
	3-3	165	219
	3-4	145	194
	3-5	173	230

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